FLUIDIZED BED STEAM REFORMING ENABLING ORGANIC HIGH LEVEL WASTE DISPOSAL

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Waste streams planned for generation by the Global Nuclear Energy Partnership (GNEP) and existing radioactive High Level Waste (HLW) streams containing organic compounds such as the Tank 48H waste stream at Savannah River Site have completed simulant and radioactive testing, respectfully, by Savannah River National Laboratory (SRNL). GNEP waste streams will include up to 53 wt% organic compounds and nitrates up to 56 wt%. Decomposition of high nitrate streams requires reducing conditions, e.g. provided by organic additives such as sugar or coal, to reduce NOX in the off-gas to N2 to meet Clean Air Act (CAA) standards during processing. Thus, organics will be present during the waste form stabilization process regardless of the GNEP processes utilized and exists in some of the high level radioactive waste tanks at Savannah River Site and Hanford Tank Farms, e.g. organics in the feed or organics used for nitrate destruction. Waste streams containing high organic concentrations cannot be stabilized with the existing HLW Best Developed Available Technology (BDAT) which is HLW vitrification (HLVIT) unless the organics are removed by pretreatment. The alternative waste stabilization pretreatment process of Fluidized Bed Steam Reforming (FBSR) operates at moderate temperatures (650-750^{o}C) compared to vitrification (1150-1300^{o}C). The FBSR process has been demonstrated on GNEP simulated waste and radioactive waste containing high organics from Tank 48H to convert organics to CAA compliant gases, create no secondary liquid waste streams and create a stable mineral waste form.

I. INTRODUCTION

Studsvik built and tested a commercial Low-Level Radioactive Waste (LLRW) FBSR Processing Facility in Erwin, TN, in 1999 [Ref. 1]. In January 2000, the throughput rate was increased and commercial operation commenced [Ref. 2]. The Studsvik Processing Facility (SPF) has the capability to safely and efficiently receive and process a wide variety of solid and liquid LLRW streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions with contact radiation levels of up to 100R/hr. The licensed and heavily shielded SPF can receive and process liquid and solid LLRWs with high water and/or organic content.

The Erwin facility employs the THermal Organic Reduction (THOR^{sm}) process, developed by Studsvik, which utilizes pyrolysis/steam reforming technology. THOR^{sm} reliably and safely processes a wide variety of LLRWs in a unique, moderate temperature (~700°C), dual-stage, pyrolysis/reforming, fluidized bed treatment system. The reforming process has demonstrated effectiveness in volatilizing/combusting organics and separating sulfur and halogens from inorganic waste materials. Of special relevance is the capability of the THOR^{sm} technology to convert nitrates to nitrogen and sodium salts to sodium compounds that are suitable for direct disposal and/or subsequent vitrification.

In February 2002, THOR^{sm} demonstrated the capability of producing sodium aluminosilicate waste forms for Hanford's sodium-bearing low activity waste (LAW) [Ref. 3]. Non-radioactive simulants of 8.1M Na+ were successfully tested in a 6-inch pilot scale facility that was located at Hazen Research in Colorado. Other demonstrations performed by Hazen showed that LAW waste could be transformed into Na_2CO_3, $NaAlO_2$, or Na_2SiO_3 feed material for the LAW Hanford melter. Addition of no solid co-reactant will yield a sodium carbonate product. Sodium combines with carbon dioxide in the reformer gases to provide a sodium carbonate product. The generation of sodium carbonate in this type of application has been studied since the 1950s in fluid bed denitration systems [Ref. 2]. Addition of a $Al(OH)_3$ co-reactant will provide an $NaAlO_2$ product, addition of SiO_2 will provide an Na_2SiO_3 product. Addition of kaolin clay will provide an $NaAlSiO_4$ product. The latter has been shown to perform well as a final waste form [Ref. 4, Ref. 5]. Testing on Hanford LAW surrogates has shown that over 95% of the sulfur compounds, fluorides and chlorides in the waste feed react in the steam reformer with the clay co-reactant and become an integral part of the final $NaAlSiO_4$ waste product's crystalline structure [Ref. 2].

In November 2002, THOR^{sm} was contracted to demonstrate the FBSR technology to produce a final

waste form for Idaho National Engineering and Environmental Laboratory acidic and radioactive Sodium-Bearing Waste (SBW) [Ref. 3]. This demonstration successfully converted the high sodium waste to an Na_2CO_3 product that met the Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WAC) for transuranic (TRU) waste. During the demonstration data were collected to determine the nature and characteristics of the product, the operability of the technology, the composition of the off-gases, and the fate of key radionuclides (cesium and technetium) and volatile mercury compounds. The product contained a significant fraction of elemental carbon residues. Mercury was quantitatively stripped from the product but cesium, rhenium (Tc surrogate), and the heavy metals were retained. Nitrates were not detected in the product and NOX destruction exceeded 98%. The demonstration was considered successful and no bed agglomeration was experienced [Ref. 3]. The steam reformer off-gas was monitored and it was determined that no O_2 was present. The offgas was mostly (76%) H_2O (wet, N_2-free basis). CO levels averaged 1.3%, while the measured CH_4 levels averaged 0.1. The O_2 and H_2 levels in the off-gas were low enough that they did not pose a significant threat of forming an explosive mixture.

The durability of the mineral waste forms produced in 2003 and 2004 during three different pilot scale FBSR demonstrations at the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) facility was evaluated by SRNL (Ref. 6). The pilot tests were performed at the STAR facility by a team of scientists from STAR, INL, and THOR^{sm} Treatment Technologies (TTT) personnel. The waste forms studied included granular mineral material produced in the fluidized bed after steady state operations were achieved and the finer mineral material from the filter (fines). Bed material from a 2003 STAR pilot scale campaign with INL Sodium Bearing Waste (SBW) was tested using ASTM C1285 (the Product Consistency Test). The durability of the bed and fines products from the STAR LAW demonstration were compared to the durability of the be and fines products from a Hanford AN-107 demonstration performed by Studsvik, Inc. at Hazen Research in Golden, Colorado. All the FBSR products, (bed and fines) evaluated in the SRNL PCT Testing were two orders of magnitude more durable than the Hanford LAW glass requirement of 2 g/m^2 release of Na^+. The PCT responses for FBSR samples tested were comparable and consistent with results from previous FBSR Hanford AN-107 product testing.

The FBSR mineralization for high organic and nitrate simulated waste streams containing high concentrations of cesium and strontium for GNEP has been demonstrated by Savannah River National Laboratory in crucible tests (Ref. 7). Most recently, SRNL has completed FBSR crucible tests in shielded cells on Tank 48 radioactive waste well characterized (Ref. 8).

II. TANK 48 SIMULANT TESTING RESULTS

The FBSR mineralization for high organic and nitrate simulated waste streams containing high concentrations of cesium and strontium using a Tank 48H simulant has been demonstrated by Savannah River National Laboratory in crucible tests (Ref. 9).

II.A. Experimental

A simulant of the Tank 48H radioactive waste was prepared based on the analytical results (Ref. 8) and used for FBSR crucible testing (Ref. 9). This slurry has approximately 13.7 wt% solids after the potassium tetraphenolborate (KTPB) precipitation was complete. In order to make a minimum of 30 grams of solid product, a test batch consisted of 218.66 grams of simulant to which 5 wt% Fe2O3 was added as $Fe(NO_3)_3 \cdot 9H_2O$ (0.38gms). Antifoam (IIT Corp. B52) was added at 100 ppm antifoam per wt% solids (Ref. 10) or 0.21 grams per batch. The Fe_2O_3 was added to provide an indicator of the REDuction/OXidation (REDOX) equilibrium that the sample experienced in sealed crucibles inside the oven. Having ~ 5 wt% Fe_2O_3 present enabled the Fe+2/ΣFe ratio of the solid product sample to be measured from which the oxygen fugacity of the reaction atmosphere could be determined. All samples were sent to the Savannah River Technology Center (SRTC) Mobile Laboratory (ML) for Fe O_2 f+2/ΣFe analysis by the Baumann method (Ref. 11,Ref. 12).

The T48H simulants were batched into stainless steel beakers. The slurry was carbonated with dry ice to convert the NaOH to Na_2CO_3 until a pH of ~9.5 was reached. This "acidification" from pH 13.3 to 9.5 also minimized foaming of the slurry. This ensured that once the carbonated material was put into a sealed crucible that a CO_2 atmosphere would be maintained. This served to duplicate the control of the atmosphere in the FBSR with CO_2 gas. The reductant of choice was sucrose. A test matrix was developed that varied three different levels of reductant based on the following stoichiometric equations:

Equation 1: $C_{12}H_{22}O_{11} + 9.6NaNO_3 \rightarrow 7.2CO_2 + 11H_2O + 4.8Na_2CO_3 + 4.8N_2$
Equation 2: $C_{12}H_{22}O_{11} + 16NaNO_2 \rightarrow 4CO_2 + 11H_2O + 8Na_2CO_3 + 8N_2$

Where the stoichiometric ratio of [C]:[N] for nitrate species is 12/9.6=1.25 (Equation 1) and 12/16=0.75 for nitrite species (Equation 2). The desired [C]:[N] ratio is 0.97 which is computed by adding the following two

terms together: 1.25 times the moles of NO_3 from all sources plus 0.75 times the moles of NO_2 from all sources for 0.22 L (the size of a sample batch) of the simulant and the $Fe(NO_3)_3 \cdot 9H_2O$ added as a REDOX indicator. The final moles of sucrose to add was then calculated as follows:

Sucrose (M) = (Desired stoichiometric factor)*([C]:[N] ratio of 0.22L feed)*(moles NO_3+NO_2 in feed)/12

In the test matrix, three different levels of sucrose (none, ½X stoichiometric, and 1X stoichiometric) and three different reaction times (1/2 hour, 3 hours, and 48 hours) were tested. The reaction times in a static crucible that could reproduce the chemistry of an active FBSR environment was a complete unknown. High purity (99.999%) Al_2O_3 crucibles were used to simulate Al_2O_3 bed material and to determine if the FBSR product was adhering to the simulated bed media. Temperatures of 650ºC and 725ºC were tested to see which levels of reductant optimized the Water Gas Shift Reaction (WGSR) (Equation 3) at which temperatures.

Equation 3: H2O (g) + CO (g) → H2 (g) + CO2

The known melt temperatures of alumina containing FBSR products are high. Nepheline ($NaAlSiO_4$) melts incongruently to carnegieite at 1280°C which then does not melt until 1526°C, if pure. The FBSR $NaAlO_2$ has a known melt temperature of 1680°C, if pure. The melt temperatures may be 100-200°C lower if other alkali or alkaline earth or iron substitutions are incorporated into the FBSR sodium aluminate containing products. The high melting temperature, refractory nature of these FBSR products was felt to be inappropriate for subsequent processing of the Tank 48H FBSR product in DWPF, e.g. high Al_2O_3 containing FBSR products could impact DWPF's melt rate and attainment rate. Hence, the lower melting Na_2CO_3 and Na_2SiO_3 FBSR products were targeted for study. Since the feed was already carbonated nothing needed to be added to the samples to optimize the Na_2CO_3 product. Precipitated silica was added to the tests where the desired final FBSR product was Na_2SiO_3 or Na_4SiO_4.

The carbonated slurries were dried to peanut butter consistency. This ensures that some H2O remains in the sample to create steam for the WGSR. Sealed crucible reaction is achieved by sealing Al_2O_3 crucibles with nepheline ($NaAlSiO_4$) gel that melts at a temperature lower than that at which the WGSR occurs. This causes the crucible to seal before the slurry reacts so that air inleakage does not occur during reaction. This is extremely important as air inleakage will alter the reactions as monitored by the measured REDOX ratio, $Fe^{2+}/\Sigma Fe$, and allow oxidizers and reductants to escape rather than reacting with the species in the slurry and additives.

The sealed samples were placed in a calibrated furnace at the test temperature designated in the test matrix. This generated a combined atmosphere of steam, CO from decomposition of the sucrose, and CO_2 from decomposition of the Na_2CO_3 formed during carbonation thus duplicating the CO-steam environment necessary for the WGSR (Equation 3) and CO_2. The furnace was purged with 99.99% Ar to ensure that no O_2 mixed with any H2 that diffused through the crucible seal thus eliminating any concern of explosive gas mixtures and duplicating the deoxygenated high CO_2 atmosphere of the FBSR process.

Samples were analyzed by X-ray diffraction (XRD) to determine if the desired FBSR product was achieved. Samples were measured by High Pressure Liquid Chromatography (HPLC) after digestion to determine if the KTPB was adequately destroyed by the FBSR reactions. Secondary reaction products such as 3PB and 2PB were also analyzed for. Total carbon (TC), Total Inorganic Carbon (TIC), and Total Organic Carbon (TOC) were also analyzed. Samples were measured for $Fe+2/\Sigma Fe$ in duplicate to determine the O_2 *f o*f the atmosphere inside the Al_2O_3 crucible during reaction. Samples were measured by Ion Chromatography (IC) for NO_2, NO_3, F, Cl and SO4 to determine the fate of these anions and the percent nitrate destruction. For those samples that the desired FBSR product was a silicate, samples were were dissolved using a LiBO2 fusion and the solution analyzed by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) for Na, K, and Si to determine if the correct ratios of silica additive had been achieved during experimentation.

II.B. Results

Due to the static nature of the environment inside the crucibles compared to the active environment of a steam reformer, most of the crucible FBSR samples were stratified and thus inhomogeneous. Reaction times of 48 hours produced the most homogeneous, least stratified, and best-reacted, samples. Samples were ground and mixed to homogenize them before any analyses were performed.

II.B.1. Baseline Testing

A sample (T48-0) was tested as a baseline. The T48-0 sample was carbonated, antifoam and $Fe(NO_3)_3 \cdot 9H2O$ were added, and the sample was dried at 60°C. This sample was analyzed for TPB by HPLC, for anions, for TC, TIC, TOC and REDOX as a baseline case. These analyses demonstrated that there was 95,100 ug/g of TPB present in the samples after the carbonation and drying steps. The presence of the TPB was also confirmed by the

measurement of TOC in sample T48-0 which showed that 19,500 ug/g of organic carbon that was present in the sample. Anion analysis of the base case indicated <100 ug/g of NO_2 and a NO_3 content of 163,000 ug/g or 16.3 wt% . This number was used with the rest of the measured NO_3 data to calculate the NO3 destruction values.

II.B.2. Teraphenylborate Destruction

Samples were tested at two different temperatures, 650°C and 725°C. Tetraphenylborate (TPB) was completely destroyed in all the samples tested, e.g. the TPB, 2PB and 3PB were all <5ug/g indicating that the thermal treatment destroyed all the TPB and its derivatives. This was confirmed by the TOC analyses for all the samples thermally treated, <100 ug/g of TOC. This indicates that FBSR is a viable technology for destruction of the organics in Tank 48H.

II.B.3. Carbonate FBSR Products

For all of the FBSR simulated samples in which the desired product was Na_2CO_3 (samples T48-1 through T48-5B and T48-13), analysis by XRD indicated that a mixture of $Na_2CO_3 \cdot H_2O$ and Na_2CO_3 was formed regardless of temperature and residence time in the furnace. However, for the T48-13 sample that was heated at 650°C for 48 hours, the XRD analysis indicated no minor constituents. This meant that the minor constituents that had appeared in the same sample reacted for only 3 hours were due to incomplete reaction. Test T48-5B or T48-13 appeared optimal for making the Na_2CO_3 FBSR product at 650°C, 1X stoichiometric sugar and 3-48 hour residence time as no minor phases were identified as incomplete reactants. Only the two primary phases Na_2CO_3 and $Na_2CO_3 \cdot H_2O$ were present in the T48-5 and T48-13 samples.

II.B.4. Silicate FBSR Products

In the current study Na_4SiO_4 was chosen as the FBSR phase of choice because it melts at ~1120°C and can only coexist with a liquid phase down to temperatures as low as 1040°C. This choice was made to limit any potential liquid phase in the steam reformer that might cause bed agglomeration. Na_2SiO_3 may be acceptable for use as feed in the DWPF as its melting temperature is ~1080°C but it can coexist with a Na_2O-SiO_2 liquid phase that melts as low as 825°C and may cause bed agglomeration. Sodium silicate (Na_2SiO_3) was the silicate FBSR product phase made by THOR^{sm} in their pilot scale Studies with Hanford's high Na+ containing Low Activity Waste (LAW).

For all of the simulated FBSR samples in which the desired product was Na4SiO4 with a Na_2O:SiO_2 ratio of 2:1 (T48-6 through T48-12), a potassium aluminosilicate zeolite phase known as faujasite ($K_{48.2}Al_{48.2}Si_{143.8}O_{384} \cdot 243H_2O$) was identified by XRD and a sodium silicate of a 1:1 Na_2O:SiO_2 stoichiometry had formed. Excess SiO_2 does not appear on the XRD pattern since the precipitated SiO_2 that was added to the sample is amorphous and will not give an XRD signal. It was apparent that the faujesite was consuming some of the SiO_2 that was meant to form the 2:1 sodium silicate phase.

Subsequent testing (T48-14) was designed to compensate for the silica being consumed by the faujesite. X-ray Diffraction analysis indicated that the major phases in the T48-14 sample after a 48 hour residence time were indeed the faujasite and the 1:1 Na_2O:SiO_2 phase. Another test (T48-15) that was designed to make the sodium silicate with a 1:1 stoichiometry of Na_2O:SiO_2 , gave an XRD pattern for yet another sodium silicate with a Na_2O:SiO_2 stoichiometry of 1:2 ($Na_2Si_2O_5$). This sample also had unreacted Na_2CO_3 present and presumably XRD amorphous SiO_2.

Analysis of all the silicate FBSR products was performed to determine if the correct ratios of Na_2O:SiO_2 had been added during experimentation. These analyses indicated that some of the Na_2O:SiO_2 ratios measured were biased low by ~20%. This may be because the precipitated silica contains absorbed water that was not factored into the batching calculation.

Even at 48 hours residence time (samples T48-12, T48-14, and T48-15) not all of the sodium carbonates present in the silicate FBSR samples converted to sodium silicate. The XRD spectra indicates the presence of carbonate phases and the high concentrations of TIC indicate large quantities of unreacted carbonate. Thus, incomplete reaction of the carbonates and silica is occurring at reaction temperatures of 650-725°C even with finely precipitated silica. Higher temperatures and the presence of excess SiO_2 may be necessary to force the final conversion of the carbonates to silicates under FBSR conditions.

In summary, if a silicate FBSR phase was desired, a silica FBSR phase was the major phase formed with carbonate and faujesite always present. Although the exact Na_2O:SiO_2 ratio of the desired FBSR silicate phase was never achieved due to incomplete reaction and silica deficient starting mixtures, this would not hinder the usage of any sodium silicate FBSR material made from Tank 48H slurry in DWPF. Achieving the desired Na_2O:SiO_2 ratio for silicate based FBSR products needs further optimization.

II.B.5. Nitrate and Sugar Destruction

In the sample test matrix, samples with the designation of B indicate comparison of tests at the two

different reaction temperatures. These were designed into the test matrix to test the optimum NO_3 destruction at the various temperatures, e.g. optimize the WGSR. Hence samples T48-2B, 5B, 7B and 10B were tested at 650°C while samples T48-2, 5, 7, and 10 were tested at 725°C.

For two of the pairs of samples tested at the different temperatures, T48-2 and 2B and T48-5 and 5B, the desired FBSR product was Na_2CO_3. Samples T48-2 and T48-2B had no sugar and samples T48-5 and T48-5B had 1X stoichiometric sugar. Comparison of the XRD spectra of the two tests without sugar demonstrates that the FBSR products in the absence of sugar includes undecomposed $NaNO_3$ which indicates that nitrate destruction is incomplete when sugar is absent at 650°C and 725°C, e.g. when sugar is absent there is no CO to optimize the WGSR. This is confirmed by the nitrate analyses and the nitrate destruction percentages which indicate that nitrate was not destroyed at either temperature for samples T48-2 and T48-2B. For the sample pair T48-5 and T48-5B sucrose was present at 1X stoichiometry. These samples had 99.1% and 97.5% NO_3 destruction at the 650°C and 725°C temperatures respectively. This indicates that the WGSR may be better optimized at 650°C than at the 725°C. Likewise, the TOC analyses indicate no residual TOC in the form of sucrose in the samples and the XRD spectra did not indicate any residual $NaNO_3$.

For two of the pairs of samples tested at the different temperatures, T48-7 and 7B and T48-10 and 10B, the desired FBSR product was a sodium silicate. Sample T48-7B had no sugar and Sample T48-10B had 1X stoichiometric sugar. Comparison of the XRD spectra of the two tests without did not show any undecomposed $NaNO_3$ but the nitrate analyses indicate that considerable NO_3 remains in the samples without sugar. The nitrate destruction percentages for these samples indicate that nitrate was only partially destroyed at either temperature for samples T48-7 and T48-7B, e.g. 41.4% and 63.3% at the lower and higher temperatures, respectively. For the sample pair T48-10 and T48-10B sucrose was present at 1X stoichiometry. These samples had 98.7% and 94.1% NO_3 destruction at the 650°C and 725°C temperatures respectively. This again indicates that the WGSR may be better optimized at 650°C than at the 725°C. Likewise, the TOC analyses indicate no residual TOC in the form of sucrose in the samples and the XRD spectra did not indicate any residual $NaNO_3$. The small amount of TOC measured in all the samples indicates that at ½ to 1X sugar stoichiometry, most of the sugar and char are consumed during denitration and that the FBSR product should not be overly reducing and thus compatible with DWPF processing of the FBSR product.

II.B.6. Particle Aglomeration

No adherence of the silicate or carbonate phases onto the Al2O3 crucibles was noted in any of the tests. Therefore, if the FBSR bed media used is, Al2O3, there should be little sticking and particle agglomeration regardless of whether the FBSR product is carbonate or silicate. This also indicates that the Na2SiO3 phase that was produced most often as an FBSR product in this study appears to be an acceptable FBSR product phase. This was confirmed by the pilot scale testing completed by THOR^{sm} on the Hanford AN-107 simulant.

II.B.7. FBSR Product Melt Temperatures

FBSR product samples T48-5B (Na2CO3 made at 650°C), T48-10 (mixed Na2CO3 and Na2SiO3 and faujesite), and T48-11 (Na2SiO3 and faujesite) were measured by Differential Thermal Analysis (DTA) to determine their melting temperature. The melt temperatures were 980°C, 1022°C, and 1049°C, respectively. These melt temperatures are all compatible with melting of these phases in the DWPF although the presence of carbonate on pre-melter processing in the Slurry Receipt Adjustment Tank (SRAT) and alteration of the DWPF frit composition to accommodate these species is still necessary.

II.B.8. REDOX Measurements and the Water Gas Shift Reaction (WGSR)

The average REDOX ratio for the 15 FBSR reactions at 725ºC are -log = 9.69 (or log = -9.69) while the average –log values for the 4 FBSR reactions at 650ºC are 10.75 (or log = -10.75). These negative log values mean that no oxygen was present during the FBSR reactions. The use of the REDOX measurements and approximations, therefore, confirms that highly deoxygenated conditions were achieved and that the crucible studies simulated the WGSR conditions.

II.B.9. Volume Reduction with FBSR Product addition to DWPF Feed

The 250,000 gallons of T48H slurry should make ~29,470 gallons of solid FBSR Na2SiO3 solid product or ~26,246 gallons of solid FBSR Na2CO3 solid product for subsequent treatment in the DWPF. This is an 88 and 90% volume reduction. This calculation assumes a final FBSR product density of 1.46 g/cc which was the number measured for the Na2CO3 solid FBSR bed product by INEEL (Ref. 3).

III. GNEP WASTE SIMULANT TESTING RESULTS

The FBSR mineralization for high organic and nitrate simulated waste streams containing high concentrations of cesium and strontium for GNEP has been demonstrated by Savannah River National Laboratory in crucible tests (Ref. 7). As part of the United States Advanced Energy Initiative, the Department of Energy (DOE) has launched the GNEP Technology Demonstration Program (TDP). The GNEP-TDP will demonstrate technologies needed to implement a closed fuel cycle that enables recycling and consumption of spent nuclear fuel in a proliferation-resistant manner. Several different flowsheets are being considered for the separation of the principal heat-generating isotopes Cs-137 and Sr-90 from the wastes generated from energy production. These isotopes will be separated and stabilized into a single waste form along with Rb and Ba* and stored at a special facility where the isotopes will be allowed to decay for approximately 10 half lives.ξ This strategy would relieve the federal geologic repository of the anticipated short-term (300 year) heat load. The repository volume will be used less efficiently if heat-producing waste forms (such as those continuing Cs-137 and Sr-90) are geologically disposed. Therefore, removing Cs-137 and Sr-90 during the reprocessing stage is needed if repository space is to be conserved. Research is necessary to develop an acceptable waste form for the Cs/Sr removed. This waste form must be economically feasible and meet yet-to-be-developed technical requirements for the storage facility. If, after 300 years of storage, the waste can be classified as low-level waste (LLW), both the waste form and the disposal options become simpler. There are several challenges inherent in the Cs/Sr baseline disposal scenario which includes the ability to show that 100 years or more of institutional control is possible, that >100 years storage constitutes disposal, and that the Cs/Sr stream is not high-level waste (HLW). Alternative disposal scenarios are:

- Processing of the Cs/Sr waste after 300 years of storage to a form that is not hazardous, i.e., can pass the Toxicity Characteristic Leach Procedure (TCLP), followed by disposal at either a LLW or HLW site.

- Processing the Cs/Sr waste stream as generated to a waste form that can be disposed of at the federal geologic repository for HLW.

Mineral waste forms are more suitable for the high heat load Cs/Sr baseline waste streams. A single phase mineral waste form that could accommodate the Cs, Sr, Ba, and Rb is easier to qualify than a multiphase mineral assemblage where Cs and Rb would likely be in one phase and Ba and Sr. In multiphase mineral waste forms one must determine the partitioning of the species amongst the phases in order to qualify the waste form. Since ~53% of the Cs-137 decays to Ba-137 and ~48% of the Sr-90 decays to Zr-90, the Cs-137 host phase must also be able to accommodate the decay to Ba-137 and the Sr-90 host phase must also be able to accommodate the decay to Y-90 and ultimately Zr-90. The Ba-137 and Zr-90 decay products must be accommodated by the mineral structure so that the phase(s) do not alter in a deleterious manner, e.g. volume expansion or contraction. This can only be simulated by demonstrating that phase pure balanced crystal-chemical substitutions of the Cs/Sr and the Ba/Zr decay products are *possible*, e.g. determine the maximum solubility of Ba in single phase $CsAlSi_2O_6$ (pollucite) or some other mineral host and/or by subjecting single phase $CsAlSi_2O_6$ to accelerated radiation treatment to induce the Cs-137 to Ba-137 transformation.

The scope of the SRNL study was to examine a variety of clays that would react with the simulated Cs/Sr GNEP streams to form an acceptable single mineral host phase or a multiphase mineral phase assemblage. Due to the high nitrate and organic content of the Cs/Sr GNEP streams, and the volatility of Cs-137 when processing, the advanced FBSR technology which limits process temperatures to 650-750°C and is CAA compliant was examined extensively.

III.A. Experimental

Simulants of three GNEP process waste streams were prepared and analyzed. Two were high organic and one was high nitrate. One of the high organic simulants known as the Engineering Alternative Study (EAS) stream and the high nitrate stream known as the Fission Product EXtraction (FPEX) stream were tested with a variety of clays and zeolite precursors. The clays included pure montmorillonites, bentonites (mixtures of montmorillonite and beidellite), kaolins, hectorites (Li montmorillonites), and illites. The zeolites included Linde IE-95 (a mixture of chabazite and erionite) used to extract Cs from aqueous streams and clinoptilite. The illites and zeolites were chosen because of their known preference for sorbing Cs from aqueous wastes.

The simulants were evaporated due to the low wt% solids content. Evaporation was stopped before supersaturation caused any crystalline phases to precipitate. The Mincalc-Rev.3 strategy developed at SRNL and used for pilot scale FBSR demonstrations since 2004 was employed to calculate the ratios of

* the Cs and Sr are stripped from the waste stream but the stripping agents carry along Ba and Rb in the waste stream as well. For brevity, the stream is referred to as Cs/Sr only.

ξ The half life of ^{137}Cs is 30.2 years, and the half life of ^{90}Sr is 29.1 years.

evaporated simulant to clay to form the desired phases. Two different strategies were used:

- substitution of Cs,Rb,Ba and Sr oxides (100 wt%) into one phase such as pollucite or Cs-mica
- substitution of Cs and Rb oxides (46-52 wt%) only into pollucite or Cs-mica allowing Ba/Sr oxides (48-54 wt%) to form a secondary phase such as the Ba feldspar known as celsian.

SRNL developed a laboratory scale method in 2003 to sequentially simulate the reactions that occur simultaneously during FBSR processing. The first step includes the nitrate/organic destruction, the water gas shift reactions (WGSR), and the REDuction/OXidation (REDOX) reactions. The first reaction step is performed at the nominal FBSR operation temperatures (650-725°C). The second step induces the hydrothermal synthesis of the zeolite mineral precursor phases in Parr bombs (i.e., Parr pressure vessels made of 316 stainless steel) at 90°C and the third step completes the dehydration reactions at the nominal FBSR temperatures (650-725°C). The laboratory scale methods (1 step and 3 step) have been demonstrated on Savannah River Site (SRS) wastes to duplicate these reactions sequentially rather than simultaneously and produce the same mineral phases. The results from these laboratory scale tests for FSBR carbonate and silicate based phases were verified against pilot scale testing performed at INEEL. The laboratory scale testing also showed that reactions with simulated FBSR bed materials could be duplicated and the use of an Fe^{+3} tracer in the waste form product could be used to monitor the f_{O_2}, f_{CO_2}, and f_{H_2} inside the crucibles. For example, crucible studies performed at SRNL had an $Fe^{2+}/\Sigma Fe$ ratio that indicated that the –log f_{O_2} values in the crucibles (static environment) were between -24 and -25 atmospheres. Pilot scale testing (dynamic environment) for the same feed at Hazen Research Inc. (HRI) corresponded to – log f_{O_2} values of -23 to -23.5 atmospheres which is within measurement error of the crucible studies.

The reductant of choice, when a reductant was used, was sucrose. A test matrix was developed that varied two different levels of reductant (none and 2X stoichiometric) based on equations 1 and 2. The clay/simulant/reductant slurries were dried to peanut butter consistency. This ensures that some H_2O remains in the sample to create steam for the WGSR. Water is also available from the sugar reductant upon heating at the FBSR temperatures. Sealed crucible reaction was achieved by sealing high purity (99.999%) Al_2O_3 crucibles with nepheline ($NaAlSiO_4$) gel that softens and seals at a temperature lower than that at which the WGSR occurs. This causes the crucible to seal before the slurry reacts so that air inleakage does not occur during reaction. The Al_2O_3 crucibles also simulate Al_2O_3 bed material and determine if the FBSR product was adhering to the simulated bed media.

The sealed samples were placed in a calibrated furnace at the test temperature designated in the test matrix. This generated a combined atmosphere of steam, CO from decomposition of the sucrose, and CO_2 from carbonate species in the simulant thus duplicating the CO-steam environment necessary for the WGSR. The furnace was purged with 99.99% Ar to ensure that no O_2 mixed with any H_2 that diffused through the crucible seal thus eliminating any concern of explosive gas mixtures and duplicating the deoxygenated high CO_2 atmosphere of the FBSR process.

Product samples were analyzed by X-ray diffraction (XRD) to determine if the desired FBSR product was achieved. Samples were measured for Total Carbon (TC), Total Inorganic Carbon (TIC), and Total Organic Carbon (TOC). All samples were analyzed at SRNL for $Fe^{+2}/\Sigma Fe$ ratio by the Baumann method. The samples were dissolved using a $LiBO_2$ fusion and the solution analyzed by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) for Al, Si, Na, Ti, Ba, Sr, Ti, Mn, and Zr to determine if the correct ratios of clay and simulant had been used during product formation. The solutions were also analyzed by ICP-Mass Spectroscopy (ICP-MS) for Rb and Cs. Samples were dissolved by sodium peroxide fusion with a water uptake. These dissolutions were measured by Ion Chromatography (IC) for NO_2, NO_3, F, Cl and SO_4 to ensure that nitrate destruction was complete. Due to the large number of samples generated not all samples were analyzed for every analysis described above.

III.B. Results

A single phase mineralized (Cs,K)-mica phase can be made by co-reacting illite clay and a GNEP simulated waste containing Cs, Ba, Sr, and Rb. The (Cs,K)-mica was demonstrated to accommodate up to 20% wt% of the GNEP waste species on an oxide basis. The (Cs,K)-mica has the potential to accommodate the Cs-137 transmutation to Ba-137 and the Sr-90 transmutation to Y-90 because micas with identical structures (and their Fe^{3+} analogs) are known to form. These micas are dehydroxylated and contain no H_2O or OH^- species that could generate radiolytic hydrogen. The (Cs,K)-mica can be made by the FBSR process which simultaneously destroys the organics and nitrates, does not produce secondary aqueous wastes, and is a CAA compliant technology. The FBSR process operates at 650-750°C.

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IV. TANK 48 RADIOACTIVE WASTE CRUCIBLE TESTING RESULTS

SRNL completed processing a total of four different samples of Tank 48 radioactive waste in the shielded cells for the Tank 48 Crucible Scale Fluidized Bed Steam Reformer (FBSR) project. All samples were produced using the carbonate flowsheet with added sugar as reductant and heat treatment using sealed crucibles with argon purge at 650^{o}C for at least 3 hours. The Tank 48 product samples were analyzed by XRD using 0.05 g solid and found to contain sodium carbonate as the single dominant crystalline phase. Preliminary REDOX data indicates measurable reduced iron (Ferrous Fe^{2+}) in dissolved product resulting from the feed samples spiked with ferric nitrate to target 5 wt% iron in the crucible product.

V. CONCLUSIONS

Waste streams planned for generation by the Global Nuclear Energy Partnership (GNEP) and existing radioactive High Level Waste (HLW) streams containing organic compounds such as the Tank 48H waste stream at Savannah River Site have completed simulant and radioactive testing, respectfully, by Savannah River National Laboratory (SRNL) demonstrating the acceptability of the FBSR process to produce waste forms for disposal.

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